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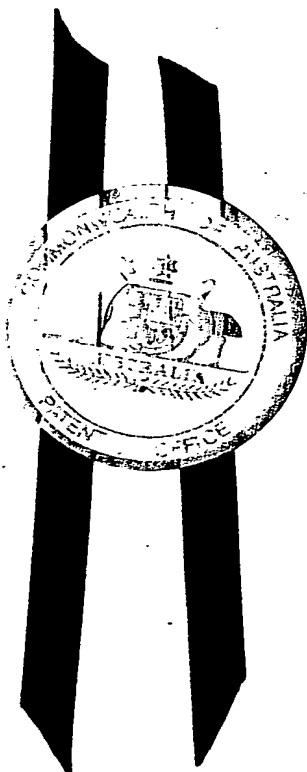
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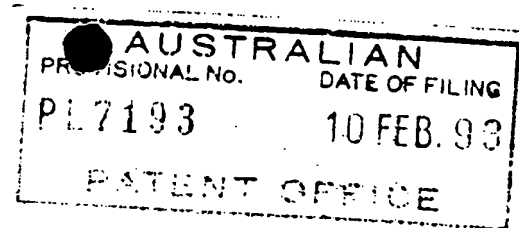
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AUSTRALIA  
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**PROVISIONAL SPECIFICATION**

**Applicant:**

TECHNOLOGICAL RESOURCES PTY LTD

A.C.N. 002 183 557

**Invention Title:**

UPGRADING TITANIFEROUS MATERIALS

The invention is described in the following statement:

UPGRADING TITANIFEROUS MATERIALS

This invention relates to the removal of impurities from naturally occurring and synthetic titaniferous materials.

5 The invention is particularly suited to the enhancement of titaniferous materials used in the production of titanium metal and titanium dioxide pigments by means of industrial chlorination systems.

10

Embodiments of the present invention have the common feature of roasting of titaniferous materials in the presence of additives and at temperatures which encourage the formation of a liquid oxide or glassy phase, followed at some stage by  
15 cooling and aqueous leaching as steps in an integrated process. Additional steps may be employed as will be described below.

20

In industrial chlorination processes titanium dioxide bearing feedstocks are fed with coke to chlorinators of various designs (fluidised bed, shaft, molten salt), operated to a maximum temperature in the range 700 - 1200C. The most common type of industrial chlorinator is of the fluidised bed  
25 design. Gaseous chlorine is passed through the titania and carbon bearing charge, converting titanium dioxide to titanium tetrachloride gas, which is then removed in the exit gas stream and condensed to liquid titanium tetrachloride for further purification and processing.

30

The chlorination process as conducted in industrial chlorinators is well suited to the conversion of pure titanium dioxide feedstocks to titanium tetrachloride. However, most other inputs (i.e. impurities in feedstocks) cause difficulties which greatly complicate either the chlorination process itself or the subsequent stages of condensation and purification and disposal of waste. The attached table provides an indication of the types of problems encountered. In addition, each unit of inputs which does not enter products contributes substantially to the generation of wastes for treatment and disposal. Some inputs (e.g. heavy metals, radioactives) result in waste classifications which may require specialist disposal in monitored repositories.

Preferred inputs to chlorination are therefore high grade materials, with the mineral rutile (at 95-96%  $\text{TiO}_2$ ) the most suitable of present feeds. Shortages of rutile have led to the development of other feedstocks formed by upgrading naturally occurring ilmenite (at 40-60%  $\text{TiO}_2$ ), such as titaniferous slag (approximately 86%  $\text{TiO}_2$ ) and synthetic rutile (variously 92-95%  $\text{TiO}_2$ ). These upgrading processes have had iron removal as a primary focus, but have extended to removal of manganese and alkali earth impurities, as well as some aluminium.

	Elemental Input	Chlorination	Condensation	Purification
5	Fe, Mn	Consumes chlorine, coke, increases gas volumes	Solid/liquid chlorides foul ductwork, make sludges	
10	Alkali & alkali earth metals	Defluidise fluid beds due to liquid chlorides,		
15		consume chlorine, coke		
20	Al	Consumes chlorine, coke	Causes corrosion	Causes corrosion, makes sludges
25	Si	Accumulates in chlorinator, reducing campaign life.	Can encourage duct blockage. Condenses in part with	May require distillation from product
30		Consumes coke, chlorine	titanium tetrachlorid e	
35	V			Must be removed, by chemical treatment and distillation
40				
	Th, Ra	Accumulates in chlorinator brickwork, radioactive; causes disposal difficulties		
45				
50				

In the prior art synthetic rutile has been formed from titaniferous minerals, e.g. ilmenite, via various techniques. According to the most commonly applied technique, as

variously operated in Western Australia, the titaniferous mineral is reduced with coal or char in a rotary kiln, at temperatures in excess of 1100 C. In this process the iron content of the mineral is substantially metallised. Sulphur additions are also made to convert manganese impurities partially to sulphides. Following reduction the metallised product is cooled, separated from associated char, and then subjected to aqueous aeration for removal of virtually all contained metallic iron as a separable fine iron oxide. The titaniferous product of separation is treated with 2-5% aqueous sulphuric acid for dissolution of manganese and some residual iron. There is no substantial chemical removal of alkali or alkaline earths, aluminium, silicon, vanadium or radionuclides in this process as disclosed or operated. Further, iron and manganese removal is incomplete.

Recent disclosures have provided a process which operates reduction at lower temperatures and provides for hydrochloric acid leaching after the aqueous aeration and iron oxide separation steps. According to disclosures the process is effective in removing iron, manganese, alkali and alkaline earth impurities, a substantial proportion of aluminium inputs and some vanadium as well as thorium. The process may be operated as a retrofit on existing kiln based installations. However, the process is ineffective in full vanadium removal and has little chemical impact on silicon.

In another prior art invention relatively high degrees of removal of magnesium, manganese, iron and aluminium have been achieved. In one such process ilmenite is first thermally reduced to substantially complete reduction of its ferric oxide content (i.e. without substantial metallisation), normally in a rotary kiln. The cooled, reduced product is then leached under 35 psi pressure at 140-150 C with excess

20% hydrochloric acid for removal of iron, magnesium, aluminium and manganese. The leach liquors are spray roasted for regeneration of hydrogen chloride, which is recirculated to the leaching step.

5

In other processes the ilmenite undergoes grain refinement by thermal oxidation followed by thermal reduction (either in a fluidised bed or a rotary kiln). The cooled, reduced product is then subjected to atmospheric leaching with excess  
10 20% hydrochloric acid, for removal of the deleterious impurities. Acid regeneration is also performed by spray roasting in this process.

In all of the above mentioned hydrochloric acid leaching  
15 based processes impurity removal is similar. Vanadium, aluminium and silicon removal is not fully effective.

In yet another process ilmenite is thermally reduced (without metallisation) with carbon in a rotary kiln, followed by  
20 cooling in a nonoxidising atmosphere. the cooled, reduced product is leached under 20 - 30 psi gauge pressure at 130 C with 10 - 60% (typically 18 - 25%) sulphuric acid, in the presence of a seed material which assists hydrolysis of dissolved titania, and consequently assists leaching of  
25 impurities. Hydrochloric acid usage in place of sulphuric acid has been claimed for this process. Under such circumstances similar impurity removal to that achieved with other hydrochloric acid based systems is to be expected. Where sulphuric acid is used radioactivity removal will not  
30 be complete.

A commonly adopted method for upgrading of ilmenite to higher grade products is to smelt ilmenite with coke addition in an electric furnace, producing a molten titaniferous slag (for

casting and crushing) and a pig iron product. Of the problem impurities only iron is removed in this manner, and then only incompletely as a result of compositional limitations of the process.

5

A wide range of potential feedstocks is available for upgrading to high titania content materials suited to chlorination. Examples of primary titania sources which cannot be satisfactorily upgraded by prior art processes for the purposes of production of a material suited to chlorination include hard rock (non detrital) ilmenites, siliceous leucoxenes, many primary (unweathered) ilmenites and large anatase resources. Many such secondary sources (e.g. titania bearing slags) also exist.

15

Clearly there is a considerable incentive to discover methods for upgrading of titaniferous materials which can economically produce high grade products almost irrespectively of the nature of the impurities in the feed.

20

The present invention provides a combination of processing steps which may be incorporated into more general processes for the upgrading of titaniferous materials, rendering such processes applicable to the treatment of a wider range of feeds and producing higher quality products than would otherwise be achievable.

25

Accordingly, the present invention provides a process for upgrading a titaniferous material by removal of impurities which process comprises the steps of:-

30

- (i) heating a titaniferous material to produce a solid titaniferous phase and a liquid oxide or glassy phase in the presence of sufficient of a compound which encourages the formation of



the liquid oxide or glassy phase at a temperature below 1300°C;

- 5 (ii) cooling the product of step (i) to form a solidified material comprising the titaniferous phase and an impurity bearing phase at a rate sufficient to ensure the susceptibility of the impurity bearing phase to decomposition in either an acid or alkaline leachant; and
- 10 (iii) leaching the solidified material in an acidic or alkaline leachant depending upon the composition of the impurity bearing phase under conditions sufficient to decompose at least a
- 15 portion of the impurity bearing phase thereby removing at least a portion of the impurities into solution.

20 In order to ensure the formation of the solid titaniferous phase and the liquid oxide or glassy phase during the heating step it will normally be necessary to add to the titaniferous material, prior to the heating step, sufficient of the compound that encourages the formation of the liquid oxide or glassy phase. However, in some cases it will not be

25 necessary since the titaniferous material itself may contain sufficient of the compound.

30 It has been discovered that the process of the invention can remove iron, magnesium and other alkaline earths, alkalis, manganese, silica, phosphorus, alumina, vanadium, rare earths, thorium and other radio active elements, which impurities form an almost comprehensive list of impurities in titaniferous mineral sources. From most materials a product purity of greater than 97% TiO<sub>2</sub> can be obtained.

Compounds added to the titaniferous material may be mixed therewith by any means ranging from direct mixing of additives prior to charging to thermal treatment to more  
5 complex feed preparations such as the formation of agglomerates or nodules of mixed products, to briquette production from feeds and additives. Many additives will be effective. In particular it is herein disclosed that sodium, potassium, lithium, phosphorus and boron compounds and  
10 minerals (e.g. borax, trona, spodumene, caustic soda) will be effective. Additives may be made individually or in combination with other additives.

Thermal processing may be carried out in any suitable device.  
15 The production of liquid phases would recommend rotary or grate kilning, but shaft furnaces may also be used and it has been found that fluidised beds can be used under some circumstances. Any gaseous atmosphere conditions may be used, from fully oxidising to strongly reducing. Thermal processing  
20 atmosphere should be chosen to most suit other steps in integrated processing. Reducing conditions may be achieved where desired by either the use of a sub stoichiometric firing flame or the addition of coal, char or coke with the thermal processing charge.

25 Thermal processing residence time at temperature will depend on the nature of the additives and the feed, as well as the operating temperature. Residence times of from 30 minutes to five hours have been effective, allowing thermal processing  
30 residence times to be set to most suit other requirements in integrated processing.

Cooling of the thermally treated material should be conducted in such a manner as to limit the reversion of the glassy

phase to crystalline phases, i.e. should be at a sufficient rate to a temperature at which the liquid glass solidifies as to ensure the formation of a solid glass rather than complete formation of crystalline products. Further, cooling should be  
5 conducted under an environment appropriate to the conditions of thermal treatment (i.e. reduction processing will require cooling in an oxygen free environment).

The aqueous leaching step need not necessarily follow  
10 directly after the presently disclosed thermal processing step. For example if the thermal processing step is conducted under oxidising conditions it may be optionally followed by a reduction step prior to aqueous leaching. Further, crushing/grinding of the thermally processed material to  
15 enhance subsequent leach performance may be undertaken.

The conditions necessary to conduct effective leaching will depend on the nature of the original feed and the additives. For example, addition of soda ash and borax to siliceous  
20 leucoxene in accordance with the present disclosure will result in a product which can be leached in sodium silicate solution formed directly from the thermally treated material; the active leachant in this case is simply water. In other cases up to 100 gpL caustic soda solution or acid will be an  
25 effective leachant. Leaching will generally benefit substantially by use of high temperature (e.g. 80 C or above), although it has not been necessary to use pressure leaching to achieve effective conditions. Nevertheless it is presently disclosed that pressure leaching can be effectively  
30 and successfully applied. Lower temperatures can also be used, although with penalties in process kinetics.

Leaching may be conducted in any circuit configuration, including batch single or multiple stage leaching, continuous

cocurrent multistage leaching, or continuous countercurrent multistage leaching. For most circumstances two stage cocurrent leaching will be most beneficial. Average residence time may vary from 30 minutes to 10 hours, depending on process conditions. Any leach vessel capable of providing adequate shear may be used. Simple stirred tank vessels are applicable.

At the conclusion of leaching the leach liquor may be separated from the mineral by any suitable means, including thickening, filtration and washing. The mineral product may then pass on to other steps in an integrated process. For example, a further acid leach may follow the disclosed leaching step, particularly where the titaniferous feed has a content of alkalis or alkaline earths.

An example of an embodiment of the disclosed processing steps into an integrated mineral upgrading process follows. Titaniferous mineral containing iron, silicon, magnesium, manganese, vanadium and aluminium is wet milled to a passing size of 100 microns and dewatered by belt filtration to 5% moisture. The dewatered mineral is fed to a high intensity mixer into which is sprayed a hot solution of sodium carbonate and borax (e.g. at 25 wt% in solution). The moist mixture is then fed to a rotary dryer wherein nodules of dried material (e.g. passing 1 mm) are formed. The dried material is mixed with a small amount of coal and recycled char and fed to a rotary kiln in which it is heated to a maximum temperature of 1000 C for residence times which avoid substantial metallisation, and then cooled in a sealed rotary cooler. The cooled material is separated from char by sizing and magnetic separation. The separated treated mineral is then leached at 100 C in a solution of sodium silicate/borax which is itself the product of the leach. After filtration

and washing the leached material is then leached with hydrochloric acid (e.g. at an acid strength of 5-10% HCl at 100 C), after which the material is washed and filtered again.

5

After such processing (optimised for a particular material) it is to be expected that removal of 98% of the contained iron, 90% of contained magnesium and manganese, 95% of contained silicon, phosphorus and vanadium and 85% of contained aluminium will have been achieved. Further, greater than 80% of contained thorium will also have been removed. The dried product will normally contain greater than 97%  $\text{TiO}_2$ .

15 The above example is only one of a number of possible schemes for incorporating the disclosed processing steps into integrated processes for the upgrading of general titaniferous materials to high grade products.

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